Multiparameter Equations of State – Recent Trends and Future Challenges (Invited)

R. Span and W. Wagner
Lehrstuhl für Thermodynamik
Ruhr-Universität Bochum
D-44780 Bochum, Germany

E.W. Lemmon
Physical and Chemical Properties Division
National Institute of Standards and Technology
Boulder, CO 80303 U.S.A.

R.T Jacobsen
Center for Applied Thermodynamic Studies
University of Idaho
Moscow, ID 83844 U.S.A.

Empirical equations of state have been developed as a very powerful tool for scientific and engineering applications. The introduction of rigorous, nonlinear multiproperty fitting has greatly improved the representation of caloric data. Together with improved experimental techniques, advanced optimization algorithms have lead to previously unattainable accuracies. The introduction of new functional forms has improved the representation of properties in the critical region. Investigations on structural features of multiparameter equations of state have improved their extrapolation behavior up to extreme temperatures and pressures. New approaches have resulted in numerically stable formulations which can be fitted successfully to substances with restricted data sets. New mixture models allow highly accurate descriptions of technically important binary and multicomponent systems. Finally, the increase in computer power and the availability of suitable software tools have dramatically increased the number of users of such equations. Even the most complex formulations, which were restricted to purely scientific use several years ago, are used in typical engineering applications today.

Currently, four subjects can be distinguished in which developments continue:

- For well measured substances, *reference equations of state* describe even the most accurate experimental results within their experimental uncertainty.
- *Equations of state for technical applications* satisfy advanced technical demands on the accuracy of thermodynamic properties, even for substances with small data sets.
- For mixtures, *Helmholtz energy based mixture models* achieve accuracies which come close to those obtained by reference equations for pure substances.
- The development of *software tools* includes recent scientific results in more and more technical applications.

These areas are by far not independent of each other and this contribution characterizes the most important trends in all four areas and points out challenges for future work. Improvements to multiparameter equations of state are always the result of extensive correlative work requiring substantial time − fast success is hardly possible. However, the capabilities of such equations and the range of their application will increase over the next few decades in the same way as it has to date.